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CONTROL OF SOOT FORMATION

FINAL REPORT

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7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED:
"Aerosol Dynamic Processes if Soot Aggregates in Laminar Flames", R. Puri, T. F. Richardson, R. J. Santoro, and R. A. Dobbins, Combustion and Flame 92, 320-333 (1993); "The Early Soot Formation in Hydrocarbon Flames", R. A. Dobbins, Glassman 70 Symposium, to appear in forthcoming Combustion Science and Technology Book Series; "Comparison of Fractal Smoke Optics Model With Light Extinction Measurements", R. A. Dobbins, G. W. Mulholland and N. P. Bryner, Atmospheric Environment 28, 889-897 (1994). "Laser Microprobe Analysis of Soot Precursor Particles and Carbonaceous Soot", R. A. Dobbins, W. Lu and R. A. Fletcher, Combustion and Flame 100, 301-309 (1995); "Carbonization Rate of Soot Precursor Particles", R. A. Dobbins, G. J. Govatzidakis, W. Lu, A. F. Schwartzman and R. A. Fletcher, Proceedings of the Third International Conference on Combustion Technologies for a Clean Environment, Lisbon, 3-6 July 1995 (submitted for publication).

Theses Awarded: "Thermocouple Thermometry in Soot Bearing Flames", G. J. Govatzidakis, Sc. B. Thesis, May 1993; "Soot Formation in Fuel-Diluted Flames", W. Lu, M. S. Thesis, July 1994; "Organic Compounds (PAH) Produced into Diesel Exhaust", M. A. Schwalm, M. S. Thesis, 1995. "Thermal Effects in the Burning of Fuel Droplets in Microgravity", N. D. Marsh, Sc. B. Thesis, 1995.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT: R. A. Dobbins, Principal Investigator; A. F. Schwartzman, Research Engineer; W. D. Lilly and P. Rush, Senior Technical Assistants; W. Lu and M. A. Schwalm, Graduate Research Assistants. (Nonsupported research contributors to the research effort were C. T. Avedisian, Visiting Professor from Cornell University; G. J. Govatzidakis and N. D. Marsh, Undergraduate Research Assistants).

9. REPORT OF INVENTIONS: None.

10. PROBLEM STUDIED: The formation of soot in hydrocarbon flames with a goal of elucidating methods of control of soot formation.

11. SUMMARY OF THE IMPORTANT RESEARCH FINDINGS:

Research on the control of soot formation in our laboratory has brought to bear three experimental techniques that have resulted in important insights into the formation of soot in combustion processes in general:

-Rapid insertion thermocouple thermometry was developed by Kent and Wagner to allow temperature measurements in soot bearing flames. The soot deposition is removed by oxidation in the outer high temperature region of the flame. Our implementation of the method gives consideration to the thermocouple time constant and the history of the temperature profile.

-Thermophoretic sampling of particles in flames was developed in our laboratory as a technique to determine the particle morphology with a minimum disturbance of this attribute. In the present investigation, this technique was used to obtain samples for chemical analysis.

-Laser microprobe mass spectrometry (LMMS) is a method of chemical analysis that gives information on chemical composition of samples as small as 10-12 gm. The ability of this technique to detect polycyclic aromatic hydrocarbons was well established in the existing literature. Furthermore, in our work the mass count has been used to deduce the H/C ratio and hydrogen mole fraction, H/(C+H), for the samples.

The early results of the LMMS analysis displayed the presence of the masses 252, 276 and 300 atomic mass units (u) as major components of the precursor particles. More recent analyses show smaller quantities of masses 302, 326, 350, 374, 398, 424, 448, 472 u in the precursor particles low in the diffusion flame. This mass sequence, with increments of 24 or 26 u, is strong evidence of the growth by the accretion of acetylene in which a fused benzenoid ring is added with, or in some cases without, the release of the H_2 molecule. Furthermore, these masses correspond to stabilomer masses found earlier by Stein and Fahr to be the most stable PAHs at flame conditions from chemical thermodynamic considerations. Finally, these results show the evolution of soot in flames is through the precursor particles composed of PAHs that undergo growth along the stabilomer ridge given by Stein and Fahr. This growth is consistent with the hydrogen abstraction, carbon addition (HACA) mechanism advocated by Frenklach.

Further implications follow from the above results. As noted by Palmer and Cullis, and since re-echoed by others, that "... the chemical structure of the starting material has little, if any, effect of the ultimate structure of the carbon formed...". It should also be noted that the 200 to 300 u PAHs have been widely found to be present in combustion processes in laboratory flames, can burners, oil-fired furnace flames, and in unsteady engine combustion processes as well. We now conclude that the route to the formation of soot is through the stabilomer PAHs that are thermodynamically favored in these diverse combustion processes.

This postulate explains the formation of the PAHs and the uniformity of the carbonaceous soot end product in the wide variety of fuels, flow fields, and combustion device geometries.

The LMMS analysis of carbonaceous soot shows the presence of many carbon clusters C_x with x ranging up to about 25, as well as C_xH_y clusters with y small at large x. The nature of LMMS response to this material is similar to its response to graphite. Thus, the precursor particles undergo a metamorphosis to carbonaceous soot as a result of the carbonization process. This process is described in the carbonization literature of Singer and Lewis as a purely thermal pyrolysis that obeys first order Arrhenius kinetics.

This background information has been used with our observations by TEM of the transformation of precursor particles to carbonaceous soot along with the measured temperature profiles, and the measured hydrogen mole fraction has been used to deduce the Arrhenius reaction rate constants to be A=1.78x10+6 s-1 and E=26.9 kcal/mole. In arriving at these values we employ our data on the particle morphology, the particle hydrogen mole fraction and also the observations of Graham et al. on the formation of soot in various hydrocarbons diluted with argon is a shock tube. We also conclude that our description of soot formation permits an interpretation of the soot shell phenomenon discovered by Avedisian et al. at Cornell when droplets are burned in reduced gravity.

The work is significant because it relates the formation of soot in diverse experiments and shows that seeming disparate results - from flames, shock tube tests, and burning droplets in microgravity - can be explained by a common set of physico-chemical concepts.

The application of these results to the engine combustion processes is being explored through a collaborative effort between the Cummins Engine Company, the National Institute for Standards and Technology and Brown University. The undersigned as the PI of the ARO grant acts as the host for this collaboration. To date samples of diesel soot from Cummins have been examined by TEM at Brown. Samples of diesel soot will soon be sent to the NIST for analysis by the LMMS. The mass spectra from these samples will be analyzed at Brown University by the undersigned.

Prepared by

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13. ABSTRACT *(Maximum 200 words)*

The personnel, publications and important research results of the three year grant on the control of soot formation are presented in this final report. Systematic probing of the ethene diffusion flame at various N_2/fuel dilution ratios using thermophoretic sampling has revealed the variation of height within the flame at which soot precursor particles are converted to carbonaceous aggregates. The measurement of temperature on the axis of the flame at various dilution ratios has been accomplished. The use of the laser microprobe mass spectrometer at the NIST to analyze the samples of soot precursor material and carbonaceous soot has provided the chemical evolution of soot in flames. These results provide the rate of the carbonization of soot precursors. The species found correspond to the stabilomers predicted by earlier thermodynamic calculations.

14. SUBJECT TERMS

Soot Aggregates, Particle Morphology, Thermophoretic sampling, Polycyclic aromatic hydrocarbons (PAHs), Carbonization rate, Soot precursor particles, Carbonaceous soot, Evolution of Soot, Laser microprobe mass spectrometry, Stabilomer PAHs.

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